sugar produces the nitriles of the two stereoisomeric monocarboxylic acids containing an additional carbon atom in the molecule. These nitriles can be hydrolyzed subsequently to the corresponding acids by an excess of hot alkali and the well-known Kiliani synthesis is then complete. We believe that the more convenient modifications used by us since 1926 to carry out these important reactions may be of general interest and therefore we describe as an example the preparation of the α- and β-glucoheptonic lactones from glucose.

Five liters of a filtered aqueous solution containing 200 g. of anhydrous calcium chloride (3.6 equivalents) and 163 g. of sodium cyanide (3.3 moles) was used to dissolve 540 g. of anhydrous glucose (3.0 moles).[4] The temperature of the solution rose from 20 to 33° within an hour and after two hours 94% of the theoretical amount of ammonia could be expelled from a sample by distillation. Thus the formation of the glucoheptonic nitriles and their hydrolysis to α- and β-calcium glucoheptonate and ammonia is quite rapid. The reaction was complete within twenty-two hours at ordinary temperature. Calcium hydroxide (222 g., 3 moles) was then dissolved in the solution and in a short while the basic calcium salts of the two glucoheptonic acids precipitated and were filtered off, washed with cold lime water until the filtrate showed only a faint chloride test, and decomposed with oxalic or sulfuric acid in the usual way. By concentrating the solution a yield of 42% of α-glucoheptonic lactone was crystallized, and a yield of 11% of the crystalline lactone of the beta acid was obtained from the residue through the brucine salt.[5] By working up mother liquors these yields were increased to 58 and 21%, respectively.

This preparative method has been applied by various workers associated with us to the conversion of xylose to gulonic lactone, lactose to a corresponding 13 carbon acid, and to the preparation of the gluco-octonic lactones. It seems to be generally the case that the basic calcium and barium salts of the monobasic sugar acids are only sparingly soluble. In the case of mannose, barium chloride was used in place of calcium chloride and the neutral barium salt of α-mannoheptonic acid, which is of low solubility and crystallizes well, could be obtained directly from the reaction mixture. It will be observed that sodium cyanide is used in the preparations in place of hydrocyanic acid, an alteration which is markedly convenient in large scale work. The preparation of α-glucoheptonic lactone from glucose is now so readily performed that it might well be used in college instruction.

The work was carried out during 1926–8 in the National Bureau of Standards and subsequently in the National Institute of Health.

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[4] One may prefer to use calcium cyanide in place of the two salts, if it is available.

[5] E. Fischer, *Ann. Chem.*, **270**, 64 (1892).

WASHINGTON, D. C.

RECEIVED MARCH 12, 1934

COMMUNICATIONS TO THE EDITOR

THE AMPHOTERIC CHARACTER OF SILVER HYDROXIDE

Sir:

A recent paper by H. L. Johnston, F. Cuta and A. B. Garrett on this subject [THIS JOURNAL, **55**, 2311 (1933)] agrees satisfactorily with the conclusions reached by E. Laue in a paper "Ueber den amphoteren Charakter des Silberhydroxyds" [*Z. anorg. allgem. Chem.*, **165**, 325 (1927)] which escaped the attention of these authors. In this paper it was pointed out that silver hydroxide is amphoteric and that the solubility product of argentic acid is about 2×10^{-18}.

Johnston, Cuta and Garrett's value 2.22×10^{-4} mole per liter for the solubility of silver hydroxide in neutral solution at 25° is not in agreement, however, with my figure of 1.36×10^{-4}, which I believe to be correct within 5%. This discrepancy would be easily understood if the water employed by Johnston and his co-workers had contained the usual equilibrium amount of carbon dioxide and had had in consequence a conductivity of 2×10^{-6} mho or more [methods for the calculation of such carbon dioxide corrections, E. Laue, *Z. anorg. allgem. Chem.*, **165**, 305 (1927)]. However, Dr. Johnston informs me that the water was of extreme purity, in which case this explanation becomes impossible. Further work on this problem is clearly necessary.

E. LAUE

RECEIVED MARCH 2, 1934

THE SOLUBILITY OF Ag_2O IN WATER AND IN ALKALI

Sir:

We regret that Dr. Laue's paper [*Z. anorg. allgem. Chem.*, **165**, 325 (1927)] was accidentally overlooked, especially since his measurements in strong alkali are roughly in agreement with our own and caused him to draw the same conclusion as ourselves respecting the existence of amphoteric properties in silver hydroxide.

We would point out that Dr. Laue's values deviate from ours not only in pure water, but to a somewhat less extent throughout the entire range of alkalinity. For this reason the agreement of his value for the activity product of the ions of argentic acid 1.96×10^{-18} with the value which may be calculated from our dissociation constant for this acid $a_{\mathrm{AgO}^-} a_{\mathrm{H}^+} = K_{\mathrm{A}} a_{\mathrm{AgOH}} = K_{\mathrm{A}} m_{\mathrm{AgOH}} = 7.9 \times 10^{-13} \times 2.5 \times 10^{-6} = 1.97 \times 10^{-18}$ must be considered as fortuitous.

After a careful study of Dr. Laue's paper we still believe that our values are nearer to the true solubilities of silver oxide in the various solutions which we have measured.

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A. B. GARRETT

RECEIVED FEBRUARY 5, 1934

PREPARATION OF CRYSTALLINE β-*d*-ALLOSE

Sir:

Levene and Jacobs [*Ber.*, **43**, 3141 (1910)] prepared sirupy *d*-allose and *d*-altrose from *d*-ribose obtained from yeast nucleic acid but were unable to obtain the sugars in crystalline form. Austin and Humoller [THIS JOURNAL, **55,** 2167 (1933)] have recently prepared crystalline β-*l*-allose from synthetic *l*-ribose. We have now prepared crystalline β-*d*-allose from *d*-ribose obtained from nucleic acid.

Application of the cyanohydrin reaction to 50 g. of purified *d*-ribose gave 25.5 g. of crude calcium *d*-altronate and 27.8 g. of crude *d*-allonic lactone. The latter after several recrystallizations was reduced with sodium amalgam. After converting the unchanged allonic lactone to the sodium salt and removing both the sodium sulfate and sodium allonate with alcohol, the *d*-allose crystallized from the alcoholic solution in good yield. The crude product was dissolved in a little water by warming, about three volumes of hot methyl alcohol was added, and the solution filtered through a little carbon. The sugar was allowed to crystallize, and was then filtered and washed with absolute ethyl alcohol. The *d*-allose thus purified gave a melting point (uncorrected) of 128–128.5°. *Rotation:* 1.338 g. in 25 ml. in a 2-decimeter tube at 20.1° gave the following specific rotations: 2 min. after solution, $[\alpha]_{\mathrm{D}}^{20.1}$ 0.58°; 4 min., 2.10°; 10 min., 3.26°; 20 min., 6.03°; 40 min., 9.57°; 120 min., 14.12°; 20 hrs. (constant), 14.41°. Since this sugar is the less dextrorotatory form of a sugar in the *d*-series, according to the nomenclature of Hudson [THIS JOURNAL, **31**, 66 (1909)] it is to be designated as the β-form. It is the eighth of the sixteen possible aldohexoses to be reported in the crystalline state.

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FRANCIS P. PHELPS
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RECEIVED MARCH 30, 1934

THE FORMATION OF CHLORINE HEPTOXIDE ON ILLUMINATION OF MIXTURES OF CHLORINE AND OZONE

Sir:

In a recent communication [THIS JOURNAL, **56,** 364 (1934)] we reported that when mixtures of chlorine and ozone are illuminated with blue light the observed pressure change is not sufficient to account for the amount of oxygen formed. At that time the discrepancy was attributed to the formation of chlorine trioxide which condensed on the walls of the reaction vessel. Further experiments, however, have shown that the discrepancy was much greater than could be accounted for in that manner alone. We have found it possible to isolate from these reaction mixtures a drop of colorless liquid which has been identified as Cl_2O_7. The identification consisted of measuring the vapor pressure of the substance over the range 213–268°K. and comparing the